

REMARKS

Claims 1-5, 7 and 9-20 are pending.

(a) Referring to Paragraph No. 2 at page 2 of the Office Action, Claims 7, 9 and 18-20 were rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over U.S. Patent No. 6,180,523 ("Lee") in view of U.S. Patent No. 6,335,104 ("Sambucetti"), further in view of U.S. Patent No. 5,330,088 ("Whitlow"), Japanese Patent No. 04297001 ("Aisaka") and U.S. Patent No. 6,060,176 ("Semkow").

Applicants traverse and respectfully request the Examiner to reconsider in view of the following remarks.

Claim 7 recites in relevant part ULSI wiring having a diffusion prevention layer comprising a nickel-rhenium-phosphorous (NiReP) plating film.

The Examiner cites Lee in view of Sambucetti as teaching a diffusion barrier layer comprising nickel-tungsten-phosphorous (NiWP). The Examiner acknowledges that Lee in view of Sambucetti do not teach a plating film of NiReP. (*See* Office Action at p. 4, ll. 16-17.) However, the Examiner takes the position that the disclosures of Whitlow, Aisaka and Semkow allegedly cure the deficiency of Lee in view of Sambucetti.

Applicants respectfully disagree.

The Examiner cites Whitlow as allegedly teaching that diffusion of copper into a contact can be prevented by placing an impermeable barrier layer between the braze material and the contact. In FIG. 3 of Whitlow, there is shown a copper electrode 27, a braze material 25, a nickel transition layer 33, a molybdenum barrier layer 35 and a contact 31. (*See* Whitlow at col. 3, ll. 56-60.) Further, the Examiner cites Whitlow at column 1, lines 51-65, as disclosing that the material for the barrier may be any element or alloy which does not alloy with the species that is

being prevented from diffusing into the contact material, such as tungsten (W) and rhenium (Re), among other listed elements. The Examiner asserts that it would allegedly have been obvious to one of ordinary skill in the art at the time of the invention to replace the NiWP protection layer taught by Lee in view of Sambucetti with a NiReP protection layer because Whitlow allegedly teaches that, among other elements generically listed, the elements W and Re may be used for forming a copper diffusion barrier. (*See* Office action at p. 5, ll. 1-5.)

In addition, the Examiner cites the abstract Aisaka as allegedly teaching that it was known at the time of the invention that NiReP films could be deposited by electroless plating for forming a resistor and, in addition, cites Semkow at column 5, lines 10-13 and 22, as allegedly teaching the use of a NiReP film as a corrosion protection layer.

However, the Examiner has not applied a reference that employs a NiReP film in ULSI wiring as a barrier layer between an insulating layer and a wiring layer. Further, Semkow generally discloses NiReP among a long list of other possible alloys and provides one of ordinary skill in the art with no particular reason to select a NiReP for use as a diffusion prevention layer in ULSI wiring. Further, the Examiner only appears to apply Aisaka and Semkow as support for the position that it was known in the art that it was possible to form a NiReP film. However, this fact alone does not provide one of ordinary skill in the art with any reason to select it for use in ULSI wiring for a diffusion prevention layer.

In light of the above, Applicants submit that the Section 103 rejection is improper.

Moreover, Applicants also submit that ULSI wiring having a diffusion prevention layer comprising a NiReP film provides unexpectedly superior properties as compared to ULSI wiring having a diffusion prevention layer comprising a NiWP film. In support of this position,

Applicants have attached herewith a publication by Tetsuya Osaka et al.¹ (hereinafter “Osaka et al.”) that demonstrates the unexpected superiority of using a barrier layer comprising a NiReP plating film as compared to a barrier layer comprising a NiWP plating film. The patentability of the claimed subject matter is further supported because Osaka et al. is direct comparison of the presently claimed invention to the closest embodiment shown in the art.

Referring to FIG. 5, Osaka et al. shows a comparison of various barrier films to one another. In particular, FIG. 5 shows the sheet resistance of NiWP/Cu and NiReP/Cu depending on the annealing temperature. In FIG. 5, it is apparent that the NiWP barrier layer suffers an undesirable increase in heat resistance after annealing at 200 °C or higher. A rise in sheet resistance occurs due to an interdiffusion of NiWP and Cu and, more specifically, represents that Cu starts adversely diffusing into the NiWP film.

In contrast, a similar rise in sheet resistance is not seen in the NiReP barrier layer until about 400 °C. Thus, the claimed NiReP film is clearly superior to the NiWP film in view of sheet resistance. This result demonstrates that the interdiffusion of the NiReP film and Cu is prevented up to 400 °C and, consequently, because Cu is advantageously prevented from being diffused into the NiReP film, the claimed NiReP film provides excellent diffusion prevention properties for USLI wiring.

Further, at least because the cited references do not employ or fairly suggest a NiReP film a barrier layer for preventing the diffusion of copper, Osaka et al. demonstrates that the superior

¹ Tetsuya Osaka et al., *Electroless Nickel Ternary Alloy Deposition on SiO₂ for Application to Diffusion Barrier Layer in Copper Interconnect Technology*, 11 J. OF THE ELECTROCHEM. SOC’Y C573 (2002). Each of the inventors of the present application are listed as an author of this publication. Also, Osaka et al. was made available electronically (i.e., published) on October 2, 2002 and thus is not prior art to the present application (the present application is a divisional of U.S. App. No. 10/154,812, which has a U.S. filing date of May 28, 2002).

characteristic as of the NiReP film as compared to a NiWP film would have been unpredictable to one of ordinary skill in the art at the time of the invention.

In view of the above, reconsideration and withdrawal of the Section 103 rejection of Claims 7, 9 and 18-20 based on Lee in view of Sambucetti and further in view of Whitlow, Aisaka and Semkow are respectfully requested.

(b) Referring to Paragraph No. 3 at page 7 of the Office Action, Claims 9-11 were rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over Lee in view of Sambucetti, further in view of Whitlow, Aisaka and Semkow, and further in view of U.S. Patent No. 4,424,805 ("Neary") and Vullaume et al. (Applied Physics Letters, vol. 69, pages 1646-48, 1996) described by U.S. Patent Pub. No. 2005/0056828 ("Wada").

Applicants respectfully traverse.

Neary and Vullaume do not make up for the deficiencies set forth above with respect to Lee, Sambucetti, Whitlow, Aisaka and Semkow as discussed above. Accordingly, the Claims 9-11 are patentable at least by virtue of the their dependency on independent Claim 7 and the additional elements recited therein.

In view of the above, Applicants respectfully request reconsideration and withdrawal of the Section 103 rejection of Claims 9-11 based on Lee, Sambucetti, Whitlow, Aisaka, Semko, Neary, Vullaume and Wada.

(c) Reconsideration and allowance of this application are now believed to be in order, and such actions are hereby solicited.

If any points remain in issue which the Examiner feels may be best resolved through a personal or telephone interview, the Examiner is kindly requested to contact the undersigned at the local, Washington, D.C., telephone number listed below.

The USPTO is directed and authorized to charge all required fees, except for the Issue Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any overpayments to said Deposit Account.

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Electroless Nickel Ternary Alloy Deposition on SiO₂ for Application to Diffusion Barrier Layer in Copper Interconnect Technology

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Electroless NiWP and NiReP films were investigated with the aim of application to barrier and capping layers in interconnect technology. These alloys containing a refractory metal with a high melting point were expected to have the ability to avoid diffusion of Cu into the interlevel dielectric. The composition and resistivity of these films were investigated first in order to know the relation between the composition and its thermal stability. The thermal stability was investigated by measuring the sheet resistance and the cross-sectional observation with field emission scanning electron microscope. Additionally, an electroless Ni alloy deposition on the SiO₂ layer without a sputtered seed layer was also examined by utilizing a self-assembled monolayer (SAM) as an adhesion and catalytic layer. Since an alkaline solution damaged the SiO₂ surface, a two-step process, which consists of a nucleation step performed in an acid electroless deposition bath and a barrier layer formation step carried out in an alkaline bath, is employed in order to fabricate a consistently uniform barrier film on the SAM/SiO₂ surface. It was found that the NiReP films formed on SAM/SiO₂ surfaces were stable up to 400°C, and are feasible for the barrier layer for the Cu interconnect technology.

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In conventional ultralarge scale integration (ULSI) devices consisting of aluminum wire structures, resistance-capacitance (RC) delay and electromigration are major limitations in achieving high circuit performance. In that situation, copper has been found to be an attractive candidate for the interconnection material to replace aluminum interconnections because of its lower electrical resistivity and higher electromigration resistance. The Cu interconnect technology was realized by an amazing development of the damascene process accomplished by the IBM Corporation.^{1,2} The damascene process lets us recognize not only the significance of the Cu interconnection but also the usefulness of wet processes that had been avoided by ULSI processes.

For a realization of Cu interconnection, it is essential to fabricate a superior barrier layer that prevents Cu diffusion into interlevel dielectric. Several materials, such as TaN, TiN, etc., were developed and employed in practice. At present, these barrier materials are deposited by sputtering. With an increasing degree of integration, however, difficulties have been experienced in forming uniformly thin films over fine patterned structures with high aspect ratios, because of the limitation associated with the technique of sputtering. In the case of chemical vapor deposition (CVD), it was expected that this problem could be overcome, but the CVD process is unfavorable because of the process cost.

Recently, a fabrication process of forming a barrier layer by using electroless deposition has been advanced.³⁻⁶ The electroless process is expected to offer several advantages, such as the simplicity of operation and its low cost, compared with the conventional sputtering process. Besides, the electroless deposition process is very attractive for overcoming the coverage problem that normally accompanies the sputtering technique, because it is expected to produce uniform deposits independently of the size and geometry of the structure. Although step-coverage problems may arise when high aspect ratio features are involved, the selection of suitable bath additive(s) and deposition conditions frequently makes it possible to accomplish electroless deposition of films with high uniformity and precision.

For producing an electroless barrier layer, however, a sputtered

seed layer is usually required to initiate the electroless deposition reaction,³⁻⁵ which detracts from the advantages of the electroless deposition method. If the elimination of the sputtered seed layer is achievable, the construction of all-wet Cu wiring process may be realized.

In this paper, electroless Ni-ternary alloy films, such as NiWP⁷ and NiReP,⁸ are investigated with the aim of application to the barrier layer in interconnect technology. The thermal stability of electroless NiReP barrier fabricated on a SiO₂ surface covered with a self-assembled monolayer (SAM),⁹⁻¹³ which was already reported by us in the previous article,¹⁴ is also examined. Since the electroless NiReP films could also be applied as a capping layer, the proposed method should help realize an all-wet Cu wiring process as illustrated in Fig. 1.

Experimental

Preparation of the substrates.—Studies of composition and resistivity.—For investigating the composition and resistivity of the electroless NiWP and NiReP films, a polyimide film was used as a substrate (UPIREX-40S). The substrate was ultrasonically cleaned in ethanol. Before catalyzation of the surface, the substrate was immersed in 1 M NaOH to roughen the surface, and then rinsed in Milli-Q water with the resistivity of 18 MΩ cm, which was used in

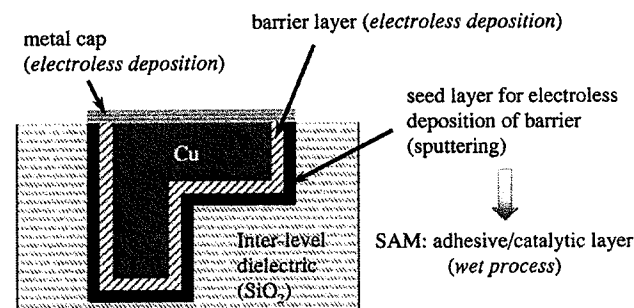


Figure 1. Schematic representation proposed for the all-wet Cu wiring process.

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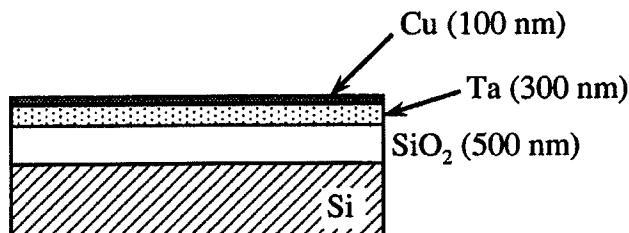


Figure 2. Schematic view of the substrate used for the investigation of thermal stability.

all stages of the experiment. The catalyzation process¹⁶ was performed by simple immersion in an aqueous SnCl_2 (0.1 g dm^{-3} of SnCl_2 in dilute HCl) followed by immersion in a PdCl_2 solution (0.1 g dm^{-3} of PdCl_2 in dilute HCl) for 1 min, respectively, and this process was repeated twice.

Study of thermal stability.—On the other hand, the substrate which has a layered structure of Cu (100 nm)/Ta (30 nm)/ SiO_2 (500 nm) on the Si wafer (Fig. 2) was used for the investigation of thermal stability, which is one of the most important factors in the barrier layer. The substrate was ultrasonically cleaned in ethanol. After cleaning, the Cu surface was subsequently rinsed in 10% H_3PO_4 and in 10% H_2SO_4 , in order to activate it. For catalyzation of the surface, the same PdCl_2 solution as that of polyimide was employed.

Formation of the alloy films on SiO_2 substrates.—In the study of electroless NiReP film on the SiO_2 layer, a CVD SiO_2 layer of 500 nm in thickness on the Si wafer was used for the substrate. The substrate was cleaned with SPM (a mixture of four parts of concentrated H_2SO_4 and one part of 30% H_2O_2) and rinsed in Milli-Q water. After cleaning, a self-assembled monolayer (SAM) of organosilane was formed on the substrate by immersion in a precursor solution of 1% aminopropyltriethoxy silane (APTES) in toluene at 60°C for 10 min. Subsequently, the substrate was ultrasonically cleaned in methanol followed by the catalyzation process. The substrate covered with SAM was catalyzed for 20 min by immersion in the solution with the composition listed in Table I.¹³

Electroless deposition.—For the electroless deposition of NiWP and NiReP, the baths listed in Table II were employed.^{7,8} To control the contents of W or Re in the electroless deposited films, the concentration of sodium citrate was varied in the range shown in the table. In the case of electroless deposition on SiO_2 , a commercial electroless NiP deposition bath (C. Uyemura & Co., Ltd., Nimuden HDX) was employed at 90°C for 15 s for a nucleation process.

Analysis.—The composition of electroless deposited films were examined by inductively coupled plasma atomic emission spectroscopy (ICP; Nippon Jarrell-Ash, ICAP-575 mark II). A four-point probe method (Kyowa Riken, model K-705RL-B) was used for measuring the resistivity. This method was also carried out for the evaluation of thermal stability by measuring the changes of sheet

Table I. Chemical compositions and operating conditions of catalytic solution.¹³

Chemicals	g/L
NaCl	0.5844
2-morpholinoethanesulfonic acid (MES)	2.132
Na_2PdCl_4	0.1140

pH 5.0 (adjusted with NaOH).

Temperature: room temperature.

Table II. Chemical compositions and operating conditions of baths.

Chemicals (mol dm^{-3})	NiWP	NiReP
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	0.027	0.075
$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	0.066	0.10
$(\text{NH}_4)_2\text{SO}_4$	0.23	-
Sodium citrate	0.068-0.20	0.10-0.40
Na_2WO_4	0.11	-
$(\text{NH}_4)_2\text{ReO}_4$	-	0.03

pH 9.0 (adjusted with NaOH).

Temperature: 90°C .

resistance by heating up to 500°C in vacuum (5×10^{-5} Torr). The thermal stability was also confirmed by a cross-sectional field emission scanning electron microscope (FE-SEM; Hitachi, Ltd., S5000).

Results and Discussion

Composition and resistivity of NiWP and NiReP films.—The composition and resistivity of NiWP films were first investigated. In this section, the polyimide substrates were used in order to measure the resistance of the alloy film itself. Figure 3a shows the composition of NiWP films formed on polyimide substrates as a function of the concentration of sodium citrate in the electroless deposition bath. Although the contents of W in the NiWP films were expected to change with the variation of concentration of sodium citrate added into the bath,⁷ the prepared NiWP film contained a little tungsten (W), around 5 wt %, and its composition was scarcely changed. With the aim of increasing the W content, the other factors which seemed to affect the film composition, such as the concentration of Na_2WO_4 and the bath pH, were also varied, but there was almost no effect on W content. Hence, the resistivity of NiWP films showed an almost constant value, as shown in Fig. 3b.

From the results of NiWP preparation, it is not anticipated that the NiWP films have excellent thermal stability against interdiffusion with Cu layer, because the W contents in the films seem to be insufficient. Hence, NiReP films, which were another candidate for the electroless deposited barrier layer, were also investigated.

Figure 4a shows the composition of NiReP films as a function of the concentration of sodium citrate. In contrast with the NiWP, the composition of NiReP films was much affected by the concentration of sodium citrate. As expected, the rhenium (Re) contents in the films increased with increasing the concentration of sodium citrate, which suggested that the film composition of NiReP could be adjusted as we hoped. In accordance with the increase of Re contents, resistivity of NiReP films drastically changed (Fig. 4b).

Effect of refractory metal codeposition on thermal stability of Ni alloy films for preventing Cu diffusion.—Based on the results discussed above, several types of films pointed out by arrows in Fig. 3a and 4a were evaluated for thermal stability by measuring their sheet resistance. An NiP film prepared from a commercial electroless plating bath was also used for comparison with the other films, i.e., NiWP and three types of NiReP films. The specimens discussed in this section were prepared on the Cu/Ta/ SiO_2 /Si substrate illustrated in Fig. 2, i.e., the alloy film was deposited on Cu like a capping layer.

In Fig. 5, sheet resistance of each film varied with annealing temperature. In the case of both NiP and NiWP films, their sheet resistance increased largely at 300°C , which suggested that the interdiffusion between Ni alloy and Cu already occurred at this temperature. On the other hand, all NiReP films were stable up to 400°C , independent of the Re content. From these results, it is apparent that the electroless NiReP films have sufficient thermal stability against interdiffusion at the Cu/barrier layer interfacial region.

The thermal stability of NiReP film was also confirmed by cross-sectional FE-SEM observation. Figure 6 shows the NiP/Cu interfa-

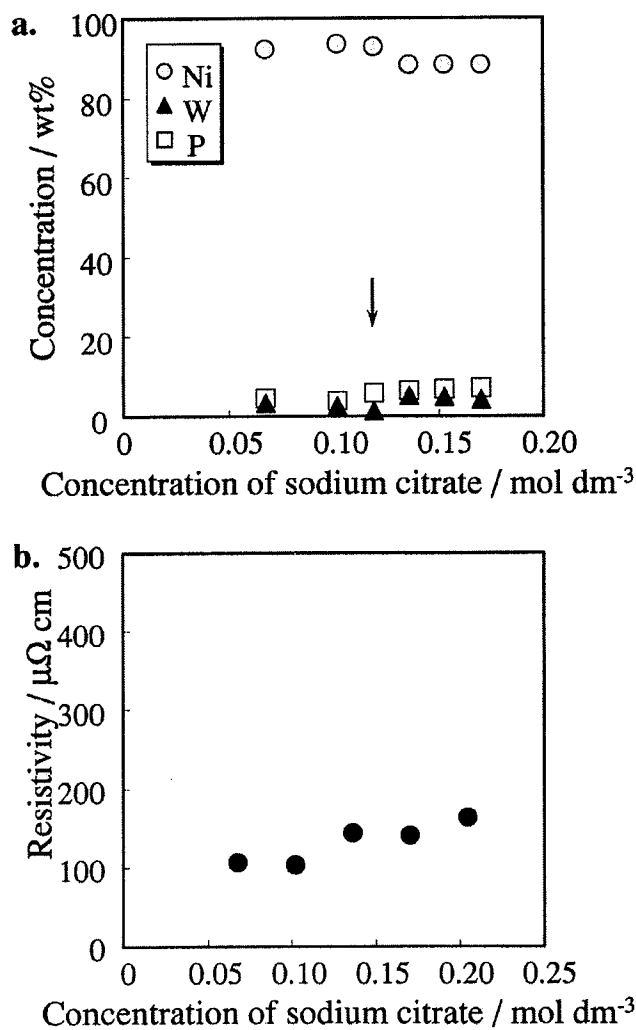


Figure 3. (a) Composition and (b) resistivity of NiWP films on polyimide substrates as a function of the concentration of sodium citrate in electroless deposition bath.

cial region. Before annealing (Fig. 6a), the interface of NiP/Cu was clearly observed. After annealing to 300°C, however, it is obvious that interdiffusion occurred in the interfacial region as observed in Fig. 6b. In contrast, the NiReP/Cu interfacial region still retained after annealing to 400°C, as shown in Fig. 7.

From the results described above, it is suggested that codeposition of refractory heavy metal is effective for the Ni-P alloy film to improve its thermal stability, but a small amount of heavy metal hardly affects the barrier property of the film.

According to the phase diagrams¹⁷ of Cu-W and Cu-Re, both of these refractory metals, W and Re, are hardly soluble to Cu. On the other hand, it is shown that Ni is easy to alloy with Cu. Although the electrolessly deposited thin films do not necessarily follow the thermodynamic equilibrium, it could be considered that the thermal stability of the electroless barrier was improved by alloying with a certain amount of refractory metal. With respect to the NiWP film, hence, there still remains a possibility for improving its property by changing W or P contents.

Electroless NiReP film on the SiO₂ substrate without sputtered seed layer.—It was suggested in the above that the NiReP films

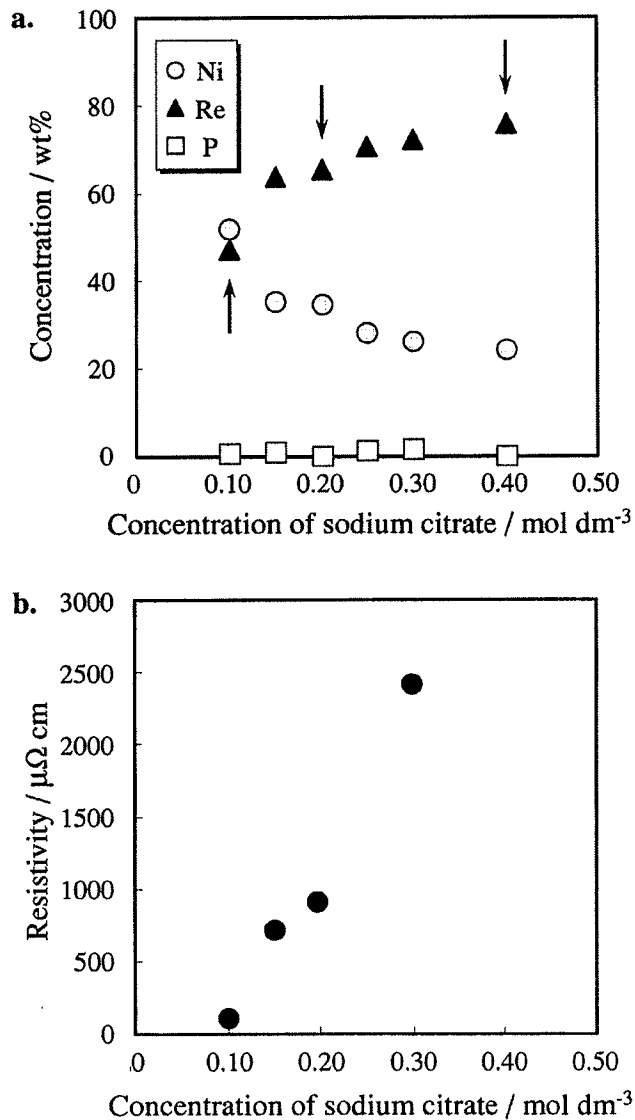


Figure 4. (a) Composition and (b) resistivity of NiReP films on polyimide substrates as a function of the concentration of sodium citrate in electroless deposition bath.

have good thermal stability and were feasible to be diffusion barriers. However, the diffusion barrier layer has to be formed on interlevel dielectrics, in this case, SiO₂.

In a previous communication,¹⁴ we proposed a fabrication process of the electroless barrier layer on SiO₂ without sputtered seed by utilizing a SAM as an adhesion/catalytic layer. Some kinds of SAMs of organosilane^{9-12,14} which have a functional group, such as amino and pyridyl groups, were utilized as an adhesion/catalyzed layer, because these SAMs seemed to be extremely effective for electroless metallization on the SiO₂ surface.¹¹ In the present study, we adopted aminopropyltriethoxy silane (APTES) in toluene for the adhesion/catalytic layer. By employing this process, we succeeded in shortening the reaction time of SAM formation, as compared to ethanol solvent (see Ref. 9). The property of toluene that hardly contains water seems to be effective for the improvement of this reaction process. In our previous experiment, we used ethanol that is easily soluble with water, which resulted in the reaction proceeding much more slowly. Besides, the reactivity of the ethoxy group in APTES with the outermost silicon atoms may also contribute to the

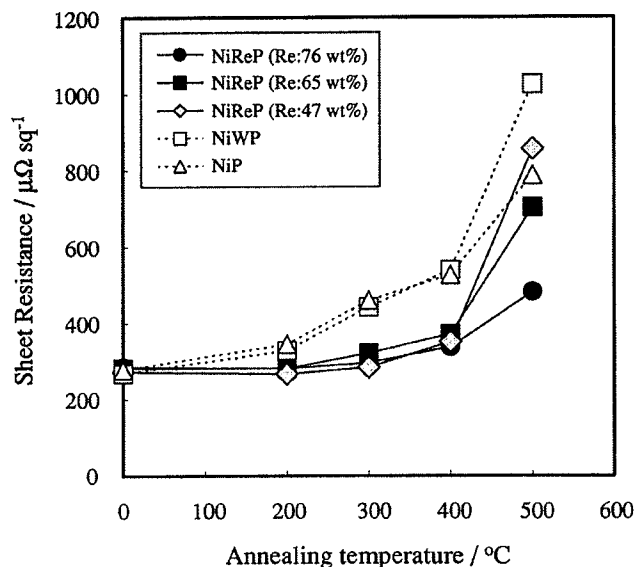


Figure 5. Variation of sheet resistance of NiReP, NiWP, and NiP films with annealing temperature. Films were formed on Cu/Ta/SiO₂/Si substrate.

improvement of SAM formation process, but this has not been clarified yet.

When the NiReP barrier layer was formed on the SAM/SiO₂ substrate, we followed a two-step process illustrated in Fig. 8 to protect the surface of the substrate from the damage caused by the

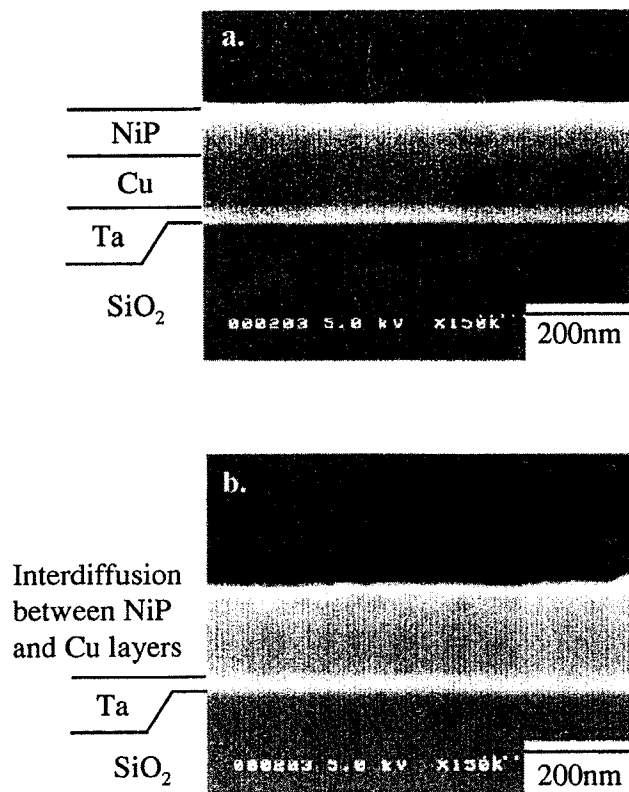


Figure 6. Cross-sectional FE-SEM images of NiP/Cu interfacial region; (a) before and (b) after annealing to 300°C.

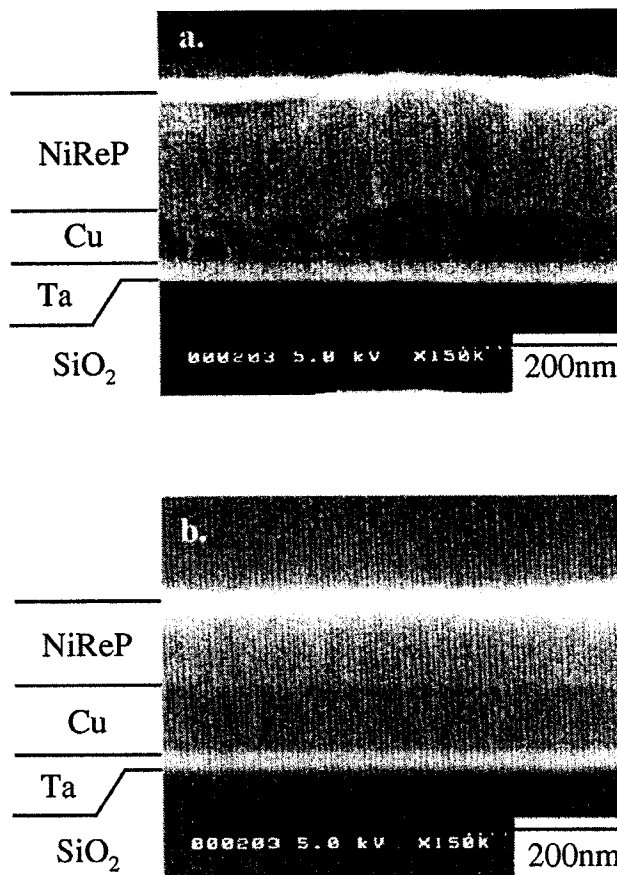


Figure 7. Cross-sectional FE-SEM images of NiReP (re: 65 wt %)/Cu interfacial region; (a) before and (b) after annealing to 400°C.

alkaline solution, *i.e.*, the electroless NiReP bath.^{14,15} In Fig. 9, the resistivity of three NiReP films on the SAM/SiO₂, formed with the aforesaid two-step process, was shown. The resistivity was increased with the concentration of sodium citrate, *i.e.*, with the increase of Re content in the film. The behavior of resistivity is almost the same as that on the polyimide substrate, but the resistivity value of NiReP on the SAM/SiO₂ surface is somewhat smaller than that on the polyimide. This result suggests that the film quality is improved by fabricating the films on a very flat substrate, SiO₂.

In Fig. 10, the thermal stability of NiReP films formed on the SAM/SiO₂ substrates were evaluated. As shown in the figure, it was confirmed that all the NiReP films fabricated with the two-step process were stable up to 400°C. The results of Auger electron spectroscopy (AES) analysis also suggested that the thermal stability of NiReP films to 400°C. These results suggest that this process is feasible for the application to the Cu wiring process. The sudden rise of sheet resistance at 500°C suggests that the NiReP barrier layer on the SAM/SiO₂ is less stable than that on the Cu/Ta/SiO₂/Si (Fig. 5), but the improvement of barrier/SAM interfacial region by optimizing the reaction condition of SAM formation works well, and the Ni nucleation on it will realize the more stable formation of a barrier layer fabricated by the electroless deposition.

It seems that this process established by the electroless deposition method and the wet chemical process of SAM formation is a promising technology for future ULSI applications.

Conclusions

The composition of NiWP and NiReP films was investigated aiming for an application to the diffusion barrier for Cu interconnect

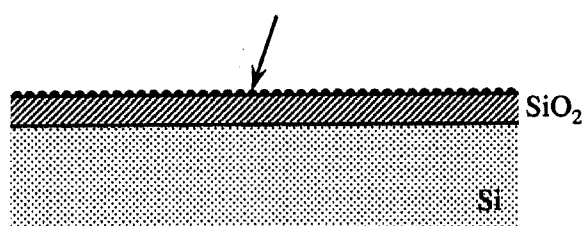
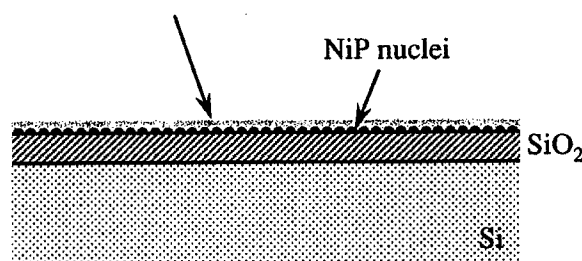
1st step;*NiP nucleation from acid bath***2nd step;***NiReP barrier formation from alkaline bath*

Figure 8. Schematic illustration of the two-step process for fabrication of barrier layer on SiO_2 . (a) The first step, formation of NiP nuclei in an acid (or neutral) bath. (b) The second step, deposition of an electroless barrier film in a basic bath.

technology. The composition of NiWP film scarcely changed, and the W content in the film was around 5%, which was not effective for the improvement of thermal stability. On the other hand, the Re content of NiReP film was changed in accordance with the concen-

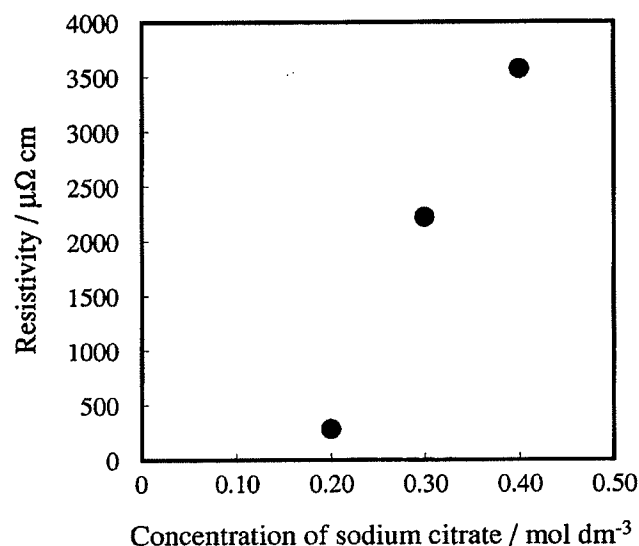


Figure 9. Resistivity of NiReP films on SAM/ SiO_2 substrates as a function of the concentration of sodium citrate in an electroless deposition bath.

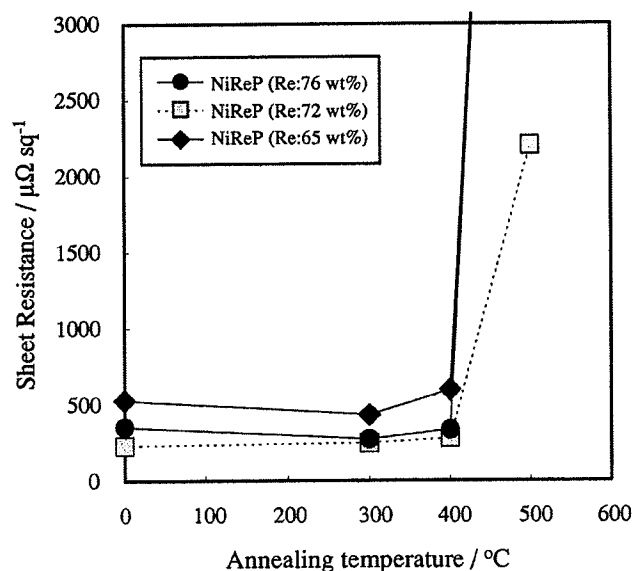


Figure 10. Variation of sheet resistance of three NiReP films with annealing temperature. Films were formed on SAM/ SiO_2 substrate.

tration of sodium citrate added into the electroless deposition bath, which meant that the Re content could be controllable. From the evaluation of thermal stability by sheet resistance measurement and cross-sectional FE-SEM observation, it was suggested that the NiReP films are feasible as diffusion barrier layers. After annealing to 400°C, the NiReP/Cu interfacial region was still retained.

Fabrication of electroless NiReP film on the SiO_2 layer without sputtered seed succeeded by utilizing the SAM as an adhesion/catalyzed layer. The reaction time of SAM formation was shortened by a little improvement in its process. For the NiReP barrier, a two-step process was adopted, which consisted of a NiP nucleation step and a NiReP barrier formation step, to prevent surface etching by alkaline solution. The thermal stability of NiReP films was also confirmed up to 400°C, when the film was formed on the SAM/ SiO_2 surface.

By the process described above, we successfully excluded several dry processes from the Cu wiring process. This achievement will contribute to the realization of the all-wet process integration in ULSI technology.

Waseda University assisted in meeting the publication costs of this article.

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